

What is claimed:

Sub
A1

1. A water- and oil-repelling adsorbing film formed on a substrate surface, said adsorbing film being a chemically adsorbed film having surface irregularities exceeding 10 nanometers, said chemically adsorbed film being bonded by covalent bonds to said substrate surface either directly or indirectly, and said chemically adsorbed film being a monomolecular or polymer film with the molecules thereof containing a fluorocarbon group and a siloxane group.

2. The water- and oil-repelling adsorbing film according to claim 1, wherein said surface irregularities are from irregularities formed on the substrate surface itself, irregularities due to fine particles formed on the substrate surface or irregularities due to fine particles present in said chemically adsorbed film.

3. The water- and oil-repelling adsorbing film according to claim 2, wherein said particles formed on the substrate surface and fine particles in said chemically adsorbed film are hydrophilic particles.

4. The water- and oil-repelling adsorbing film according to claim 3, wherein said hydrophilic particles and said polymer with the molecule thereof containing a fluorocarbon group and a siloxane group are bonded to one another by covalent bonds.

5. The water- and oil-repelling adsorbing film according to claim 1, wherein the surface irregular chemically adsorbed film is bonded by covalent bonds of $-\text{SiO}-$ or $-\text{SiN}-$ to the substrate surface.

6. The water- and oil-repelling adsorbing film according to claim 1, which comprises a thin layer of polysiloxane or a thin layer of chemically adsorbed monomolecular layer of siloxane formed on the substrate surface and a surface irregular film formed on said thin layer or said chemically adsorbed monomolecular layer.

7. The water- or oil-repelling adsorbing film according to claim 1, wherein the substrate surface is provided with irregularities formed by particles and/or a coated layer incorporating silicate glass and having surface irregularities and a thin layer or a chemically adsorbed monomolecular layer with the molecules thereof containing a fluorocarbon group and a siloxane group, said surface irregular layer and said thin layer or chemically adsorbed monomolecular layer being bonded to each other by siloxane bonds.

8. The water- and oil-repelling adsorbing film according to claim 1, wherein said substrate is made of at least a member of a group consisting of glass, ceramics, metals, plastics, wood, stone and semiconductors.

Sub
A1
Antal

9. The water- and oil-repelling adsorbing film according to one of claims 7 and 8, wherein the substrate surface is provided with irregularities at a level less than the wavelength of visible light, and which is anti-contaminating.

10. The water- and oil-repelling adsorbing film according to one of claims 7 and 8, wherein said substrate is a plastic film.

A

11. The water- and oil/repelling ~~adsorbing~~ film according to claim 10, wherein said plastic film has a coarsened surface with surface irregularities at a level less than 0.3 micrometers.

A
A

12. A method of manufacturing a water/ and oil/repelling ~~adsorbing~~ film comprising:

making a substrate surface irregular; and

contacting said irregular surface with a non-aqueous solution containing an active surface material having a fluorocarbon group and a chlorosilane group or having a fluorocarbon group and an alkoxysilane group.

A
A

13. The method of forming a water/ and oil/repelling ~~adsorbing~~ film on a substrate surface according to claim 12, comprising at least the following steps A to D:

A. forming the substrate surface having surface active hydrogen groups with surface irregularities and/or then

providing the substrate surface with active hydrogen groups;

B. contacting the substrate surface with a silane-based surface active material with the molecules thereof containing a silyl group at one end and a fluorocarbon group at the other end to adsorb said surface active material to the substrate surface by a dehydrochlorination reaction or a dealcoholation reaction;

C. forming an outer layer by reacting with water with or without previous removal of non-reacted surface active material by washing using a non-aqueous organic solution; and

D. drying or thermally treating the substrate surface.

A
A
14. The method of forming a water/ and oil/repelling ~~adsorbing~~ film on the substrate surface according to claim 12 comprising at least the following steps a to f:

a. forming the substrate surface having active hydrogen groups with surface irregularities and/or then providing the substrate surface with active hydrogen groups;

b. contacting the substrate surface with a non-aqueous solution containing a surface active material with the molecules thereof having a plurality of chlorosilyl groups to adsorb said surface active material by a dehydrochlorination reaction;

c. forming an inner layer by reacting with water with or without previous removal of non-reacted surface active

material by washing with a non-aqueous organic solution;

d. contacting the surface of said inner layer with a silane-based surface active material with the molecule thereof containing a silyl group at one end and a fluorocarbon group at the other end to adsorb said surface active material to the substrate surface by a dehydrochlorination reaction or a dealcoholation reaction;

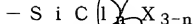
e. forming an outer layer by reacting with water with or without previous removal of non-reacted surface active material by washing with a non-aqueous organic solution; and

f. drying or thermally treating the substrate surface.

A
A
15. The method of manufacturing a water/ and oil/ repelling ~~adsorbing~~ film according to claim 12, wherein said substrate surface is provided or formed with irregularities by:

mixing fine particles and silicate glass on the substrate surface and then thermally baking said coating together with the substrate, electrolytic etching, chemical etching, sand blasting, spattering, depositing, or rubbing.

A
A
16. The method of manufacturing a water/ and oil/ repelling ~~adsorbing~~ film according to one of claims 13 and 14, wherein said chlorosilyl-based surface active material is one with the molecules thereof having at one end a chlorosilane group represented by a formula;



where n represents an integer from 1 to 3, and X represents at least one functional group selected from the group consisting of a lower-alkyl group and a lower-alkoxyl group.

17. The method of manufacturing a water/ and oil/ repelling-adsorbing film according to one of claims 13 and 14, wherein said silane-based surface active material is a compound selected from a group consisting of

$$\text{CF}_3 - (\text{CF}_2)_n - \text{T} - \text{SiY}_p\text{Cl}_{3-p}$$

where n represents an integer from 1 to 25, T represents a member of the group consisting of an alkyl group, an ethylene group, an acetylene group and a substituted group containing a silicon atom and a hydrogen atom, Y represents a substituted group selected from the group consisting of an alkyl group, a cycloalkyl group, an aryl group and derivatives of these groups, and p represents a number selected from the group consisting of 0, 1 and 2, and

$$\text{CF}_3 - (\text{CF}_2)_n - \text{T} - \text{SiZ}_q(\text{OA})_{3-q}$$

where n represents either 0 or an integer, T represents a member of the group consisting of an alkyl group, an alkylene group, an alkyne group, and a substituted group containing a silicon atom and a hydrogen atom, Z represents a substituted group selected from a group consisting of an alkyl group, a cycloalkyl group, an aryl group and derivatives thereof OA

represents an alkoxy group with A representing a hydrogen atom or an alkyl group, and q represents 0, 1 or 2.

AA
18. The method of manufacturing a water/ and oil/ repelling ~~adsorbing~~ film according to claim 14, wherein said surface active material with the molecules thereof containing a plurality of chlorosilyl groups is a compound selected from the group consisting of SiCl_4 , SiHCl_3 , SiH_2Cl_2 , and $\text{Cl}-(\text{SiCl}_2\text{O})_n-\text{SiCl}_3$, where n is an integer from 1 to 10.

AA
19. The method of manufacturing a water/ and oil/ repelling ~~adsorbing~~ film according to claim 12, wherein said substrate having hydroxyl groups at the surface is a plastic substrate with the surface thereof treated in an oxygen-containing plasma atmosphere to be hydrophilic.

AA
20. The method of manufacturing a water/ and oil/ repelling ~~adsorbing~~ film according to one of claims 13 and 14, wherein said active hydrogen group on the substrate surface is a member of the group consisting of a hydroxyl group, an amino group and an imino group.

AA
21. The method of manufacturing a water/ and oil/ repelling ~~adsorbing~~ film according to one of claims 13 and 14, wherein said non-aqueous solution containing a chlorosilyl-based surface active material contains a crosslinking agent selected from the group consisting of $\text{SiP}_s\text{Cl}_{4-s}$ where

P represents H, a lower-alkyl group and a lower-alkoxyl group, and s represents of 0, 1 and 2, and $SiQ_t(OA)_{4-t}$ where Q is at least one substituted group selected from the group consisting of a lower-alkyl group and a lower-alkoxyl group, A represents hydrogen atom or a lower-alkyl group, and t represents 0, 1 or 2.

22. A method of manufacturing a water/ and oil/
repelling ~~adsorbing~~ film comprising:

preparing a substrate having active hydrogen groups at the surface and contacting said substrate with a non-aqueous solution containing a material with the molecules thereof having a plurality of chlorosilyl groups to coat said material onto the surface of said substrate through a reaction between active hydrogen groups at said substrate surface and the chlorosilyl groups of said material with the molecules thereof having a plurality of chlorosilyl groups;

coating with a non-aqueous solution containing a mixture of the surface active material with the molecules thereof containing a fluorocarbon group and a chlorosilane group and fine particles having a hydrophilic surface;

contacting with a mixture of a material with the molecules thereof containing a fluorocarbon group and an alkoxysilane group and fine particles having hydrophilic surface; and

thermally baking said coating together with the substrate.

A
23. A method of manufacturing a water/ and oil/
repelling ~~adsorbing~~ film comprising:

a step of preparing a substrate having active hydrogen groups at the surface and contacting the surface of said substrate with a non-aqueous solution containing a material with the molecules thereof containing a plurality of chlorosilyl groups to adsorb said material to the substrate surface through a reaction between active hydrogen groups on the substrate surface and chlorosilyl groups of said material with the molecules thereof having a plurality of chlorosilyl groups;

forming a thin film or a chemically adsorbed monomolecular film of said material with the molecules thereof containing a plurality of chlorosilyl groups on said substrate with or without removal of non-reacted material remaining on the substrate by washing with a non-aqueous organic solution;

adsorbing a non-aqueous solution containing a mixture of a surface active material with the molecules thereof having a fluorocarbon group and a silyl group and fine particles having hydrophilic surface; and

thermally baking said coating together with the substrate.